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16. ABSTRACT

Exposure assessment enhanced by mathematical modeling has become an accepted technique for evaluating the environmental risk associated with the release of toxic substances into various environmental media. Mathematical models for analyzing the behavior of toxic substances in river systems range from simplified, plug-flow transport procedures to dynamic water and sediment routing procedures incorporating characterization of the physical, chemical, and biological processes that collectively determine the toxicant concentrations in time and space. Four levels of such models can be identified: (1) steady-state, constant flow; (2) plug flow, time-of-travel analytical solution; (3) quasi-dynamic routing incorporating simple sediment interaction with the bed; and (4) dynamic routing incorporating dynamic, process-oriented sediment interaction with the bed. In levels 1, 3, and 4, chemical exchange with the bed is handled as a linear dispersive interchange. In each of the four levels, sorption, volatility, hydrolysis, photolysis, oxidation, and bacterial degradation of organic toxicants are included. These four levels of models were compared by predicting pesticide fate and transport within the Yazoo River system using candidates from each level. For some cases, sediment and water were simulated. A comparison of predicted concentrations is presented and discussed.

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Introduction

Evidence of potentially harmful effects of pesticides and other toxic organic chemicals on aquatic organisms has led to intensive efforts toward environmental risk assessment for existing and new chemicals. Laboratory bioassay tests, environmental damage episodes like fish kills, and information about chemical properties have all been studied with a view toward estimating or assigning risk associated with chemical use patterns, waste discharges, and related management practices. The most direct procedure for evaluating environmental risk attendant to chemical use or release is a field study in which aquatic systems are monitored for damage, causal factors delineated, and results extrapolated or generalized. In this manner, risk is allocated based upon observed damage Another popular procedure has been allocation of risk based on observation of the chemical per se (not its effects). In this case risk is allocated based only on predictions of potential damage.

These environmental observation procedures have been effectively applied to a number of toxicant-related environmental problems, most notably those associated with chlorinated hydrocarbon pesticides. Such methods are not without their shortcomings, however. In the evaluation of observed damage, one may be able to delineate the specific causal factors but the frequency of their occurrence (and hence the

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risk or probability of their reoccurrence) cannot be discerned short of observing future episodes through numerous repeated studies. The same is true for observations of toxicant concentrations designed to infer risk or probabilities of occurrence. In both cases, observations can be made only after the chemical in question is in widespread use and discharges are identified and measured. It would seem more prudent to evaluate environmental risk of toxic organic chemicals before they are released and widely used.

Concern about pesticides and other toxic chemicals is related to effects or damage. The concept of risk reflects the likelihood of probability of such effects. Obviously, if an effect is induced, the organism affected must first have been exposed to the toxicant for a time period and intensity sufficient to inflict the damage. The study of this exposure, or exposure assessment, is defined as a quantitative evaluation of the concentration of chemical toxicants in contact with receptor populations for various environmental media as the toxicant is released, transported, and transformed among and within environmental compartments.

The source of toxic chemicals in a river basin is an important factor in the selection of techniques to analyze the problem. Toxic chemical releases may arise both from nonpoint sources such as agricultural fields from which pesticides are transported in runoff and from point sources such as chemical manufacturing plants from which chemicals are discharged in effluent. Nonpoint sources are characterized by highly variable loadings with rainfall-runoff events often dominating the timing and magnitude of chemical inputs to the receiving waters. Point sources are usually much less varied and are often thought to provide steady (not varying in time) inputs to the aquatic system. Exposure assessments for toxic chemicals in the aquatic environment must accommodate both the nonpoint or variable loading case and the point or steady loading case.

Chemical concentrations in aquatic environments are also determined by the transport and transformation processes known to occur in river basins. Chemical transport is dominated by mass movement in water or on sediment and to a lesser extent in the air by volatilization processes. As chemicals are transported by water or sediment, they are subject to a number of physical, chemical, and biological processes that can lead to either transport or transformation. In general, the influence of transport on chemical behavior is determined by the local environmental regime (flow rates, sediment concentrations, etc.); transformation processes are largely determined by chemical properties and to a lesser extent by environmental conditions.

A Mathematical Statement of the Problem

Exposure assessment as a part of risk evaluation implies the need to estimate frequency of exposure. Exposure can be viewed as the realization of the joint probability of an ambient concentration and the existence of receptor populations. The probability of ambient concentrations can be approximated by calculating their frequency of occurrence over a sufficient period of time. A convenient way to represent frequency is the cumulative distribution function (cdf). A cdf can be expressed as a graph of the concentrations (on the abcissa) exceeded for various fractions of a time period (on the ordinate). A cdf can be related to average expected return periods for different concentrations. A convenient way to quantify the ambient concentration required for environmental exposure is the cumulative frequency diagram. A cumulative frequency diagram is simply a graph of the concentration levels exceeded a given percentage of a time period. Given the cdf for a specific chemical in a specific environment, one can, for example, say that once every 10 years the concentration of a specific chemical will exceed a specified level. The concentration level can then be related to biological effects

information (e.g., LC_{50} values) and a return interval for damage (or risk) results.

A cdf can be readily constructed given sufficient data in the form of time-series chemical concentrations. Rarely are any such data available, however, and when short time periods are sampled, the statistical reliability of the resulting data is always suspect. An acceptable alternative to field sampling is mathematical modeling. With modeling, the problem of generating time-series estimates for chemical concentrations remains, however. In aquatic systems, both dissolved and sorbed chemical states are of interest. Falco and Mulkey (5), Falco et al. (6), Onishi et al. (14), and Mulkey and Falco (13) have developed and summarized the governing equations for toxicant concentrations in the water column. In the following development, it is convenient to define concentration-related symbols as in Table 1. The following longitudinal one-dimensional mass-balance equations apply.

$$\frac{\partial C_w}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C_w}{\partial x}\right) - \frac{\partial (C_w U)}{\partial x} + W \pm \sum R_j \qquad [1]$$

$$\frac{\partial C_s}{\partial t} = \frac{\partial}{\partial x}\left(D_s \frac{\partial C_s}{\partial x}\right) - \frac{\partial (C_s U_s)}{\partial x} + W' \pm \sum R_{sj} \qquad [2]$$

where C_w, C_s = concentration of constituent in the dissolved and sorbed states, respectively (M/L^3)

D, D_s = dispersion coefficient for dissolved and sorbed constituents (L^2/T)

U, U_s = flow velocity of water and sediment (L/T)

W, W_s' = source strengths of dissolved and sorbed constituents, ($ML^{-3}T^{-1}$)

R_j, R_{sj} = rate of production or elimination of dissolved and sorbed constituent by pathway j ($ML^{-3}T^{-1}$)

x = distance (L)

t = time (T)

Table 1. Concentration-Related Symbols Used in Mathematical Equations

Symbol	Definition	Units
C	Concentration of chemical (bed or water)	mgc/l_T
C_w	Concentration of dissolved chemical in water	mgc/l_T
C_w'	Concentration of dissolved chemical in water $C_w = C_w/\theta$	mgc/l_w
C_s	Concentration of sorbed chemical in water	mgc/l_T
C_s'	Concentration of sorbed chemical in water $C_s = C_s/S$	mgc/kgs
C_p	Concentration of dissolved chemical in bed (pore water)	mgc/l_T
C_p'	Concentration of dissolved chemical in bed (pore water) $C_p = C_p/\theta$	mgc/l_w
C_b	Concentration of sorbed chemical in bed	mgc/l_T
C_b'	Concentration of sorbed chemical in bed $C_b = C_b/S$	mgc/Kgs
C_2	Concentration of sediment (bed or water)	mgs/l_T
S	Concentration of sediment (bed or water) $S = C_2 * 10^{-6}$	kgs/l_T
S'	Concentration of sediment (bed or water) $S = S/\theta$	kgs/l_w
θ	Porosity, or volume water per volume segment	l_w/l_T

Equations 1 and 2 include the influence of dispersion, advective transport, sources, and sinks on the change in toxicant concentration or mass. Equation 2 is applied to the sorbed state of the constituent and hence the sediment transport must be included. Sediment movement is accounted for in three terms: U_s, the sediment velocity in the x-direction; W', the sorbed pollutant (attached to sediment) sources; and ΣR_{sj}, the sink terms for the sorbed pollutant including settling and/or resuspension.

Sediment transport is an important process in hydraulics and river mechanics, but its role in pollutant transport is not fully known. Several investigators (10,18) have shown that for most organic toxicants, particularly non-polar compounds, the sediment organic matter determines the extent of sorption and hence the importance of sorbed-pollutant transport. The particle size of the sediments is influential, but Rao and Davidson (18) have shown that the organic matter content of each size fraction is the controlling factor. Organic matter content and surface area relationships suggest that silt and clay size sediment fractions are most relevant in sediment transport. One outcome of this rationale is the idea that in river systems, wash load or suspended sediment is the important pollutant transport medium rather than bed load. If bed load transport can be ignored, the problem remains to estimate suspended sediment. For washload, the stream transport capacity typically is in excess of sediment supply, and the problem is one of estimating sediment source loading--namely, watershed erosion. Thus, the key sediment-related term in equation 2 is the source term, W'.

Bed load transport <u>per se</u> may be relatively unimportant in pollutant transport, but interaction between the stream bed and the overlying water should not be ignored. Concentration gradients between the bed material and the overlying water will result in sorption and desorption and thus the stream bed can act either as a sink or a source of contaminants. For the stream bed one can write:

$$\frac{\partial C_p}{\partial t} = \frac{\partial}{\partial y}\left(D_b \frac{\partial C_p}{\partial y}\right) - \frac{\partial (U_p C_p)}{\partial y} \pm \sum R_{pj} \qquad [3]$$

$$\frac{\partial C_b}{\partial t} = \pm \sum R_{bj} - \frac{V_s C_b}{L_s} + \frac{V_d C_s}{L_w} \qquad [4]$$

where y = vertical direction (L)

C_p, C_b = bed concentration of chemical in the dissolved

and sorbed states, respectively (M/L^3)

D_b = vertical dispersion coefficient for dissolved constituents (L^2/T)

R_{pj}, R_{bj} = rate of production (+) or elimination (-) of dissolved and sorbed chemical by pathway j ($ML^{-3}T^{-1}$)

U_p = velocity of net pore water movement into or out of the bed (L/T)

V_d, V_s = deposition and scour velocity of sediment between bed and water column (L/T)

L_w, L_s = depth of water compartment and active bed layer (L)

Equation 3 accounts for diffusion-dispersion and pore water transport of pollutants between the bed and the overlying water column. Equation 4 accounts for sediment-bound transport by including the scour and deposition terms, V_d and V_s. Estimation usually requires a rigorous treatment of hydrodynamic forces and characterization of sediments (e.g., cohesiveness). Several approaches are available for this purpose, but many chemical exposure models either omit these processes entirely or lump them into an overall calibrated dispersion or exchange coefficient.

Equations 1-4 describe the fate and transport of dissolved and sorbed pollutants, but an interaction term must be added. Specifically, the interaction of dissolved organic toxicants with entrained sediment must be accounted for mathematically. If one assumes sorption is kinetically a first order process, then a rate equation similar to the other expressions can be written as:

$$\frac{R_s}{S} = k_s C_w' - k_d C_s' \qquad [5]$$

where R_s = net rate of chemical transfer between sorbed and dissolved state, ($ML^{-3}T^{-1}$)

k_s = rate constant for sorption, ($L_w^3 M_s^{-1} T^{-1}$)

k_d = rate constant for desorption, (T^{-1})
C_s' = concentration of sorbed pesticide, (M/M_s)
C_w' = concentration of dissolved pesticide (M/L_w^3)
M_s = mass of sediment, (M)

If one assumes $R_s = 0$ then

$$k_s C_w' = k_d C_s'$$

$$\text{or} \quad C_s' = \frac{k_s}{k_d} C_s' \qquad [6]$$

Note that equation 6 is the linear form of the Freundlich isotherm with the ratio $k_s/k_d = K_d$ being the distribution (or partition) coefficient. This coefficient is known to be a function of both the toxicant and the characteristics of the sediments onto which sorption has occurred. Most organic pollutants of current interest are non-polar, hydrophobic compounds whose K_d values correlate quite well with the organic fraction of the sediment. Rao and Davidson (18) and Karickhoff et al. (10) have developed empirical expressions for estimating appropriate values.

Both pollutants and sediment can result from rainfall-runoff or point source discharges. They are estimated by a variety of methods, including models, but are assumed as given for the procedures discussed in this paper. The problem remaining in the mathematical model formulation of aquatic fate and transport, then, is definition of the transformation rates, R_j.

The rate equation for the last terms in equations 1-4 cannot be specified in a general form because, depending on the process under consideration, many variables may be influencing the rate, leading to a multi-term and often non-linear relationship. It is convenient, however, to assume the rates are first order with respect to the pollutant concentration for given environmental conditions, leading to

$$R = \sum_{j=1}^{n} k_j C \qquad [7]$$

where R = overall rate of dissipation processes or total first-order degradation rate ($ML^{-3}T^{-1}$)

k_j = first order rate constant for the jth process, which can vary in space and time (1/T)

n = number of processes operating on chemical

Only rarely does equation 7 provide a rigorous description of the kinetics of pollutant degradation in aquatic systems, but if the influencing variables that lead to more complex expressions are reasonably constant for a specific situation then the influence can be lumped into the single value, Σk_j.

Using selected pesticides several investigators have studied individual processes (11,17,22-24). Smith et al. (20) have identified the major pathways that lead to transformation of organic pollutants in the aquatic environment. The role of these processes is receiving increasing attention and laboratory protocols for related measurements have been developed (12). The general processes identified include hydrolysis, photolysis, oxidation, and microbial degradation. Additional processes that influence the transport of pesticides and other toxic substances include volatilization and sorption. These transformation processes are reviewed in detail in another paper in this symposium.

Alternative Solutions to the Problem

To estimate the frequency of occurrence of a given concentration, one would require a long time history of measured or simulated data, typically encompassing the range of the system's natural variability. In the general case, streamflow and sediment load must also be estimated, but for this analysis it is assumed that both are known. This assumption is

not unreasonable given the extent to which major river systems are gaged. Where nonpoint source loads are of major concern, simulation of flows may be preferred because the toxicant source loads and the flow (both water and sediment) originate from the same locations within the watershed. Transport processes that occur between field-sized areas and stream channels (e.g., infiltration, sediment deposition) can result in less pollutants being delivered to the stream than are delivered to the immediate field boundary. If nonpoint source loads are estimated independently from stream flow, then the usual procedure is to apply a polluant "delivery ratio" (fraction of erosion and pollutants leaving field sites that reach streams). The following alternative solution approaches assume known discharge and flows. For the nonpoint loads, delivery ratios are assumed to be unity.

Analytical Solution of Flow Equation

If equations 3 and 4 are ignored, then under certain conditions an analytical solution to equations 1 and 2 can be developed (7,13). Specifically, if dispersion is assumed to be negligible and flow velocities and sediment concentrations are set at constant values, equations 1, 2, and 5 can be solved for the pulsed loading case to yield:

$$C = C_o \exp \frac{\sum_{j=1}^{n} k_j + \sum_{j=1}^{n} k_{js} K_D S \tau}{1 + K_D S} \qquad [18]$$

where C_o = initial toxicant load or concentration (M/L^3)
k_j = pseudo-first order rate constant for the jth process for dissolved state ($1/T$)
k_{js} = pseudo-first order rate constant for the jth process for sorbed state ($1/T$)
n = total number of processes operating
K_D = distribution or partition coefficient (L^3/M)

S = suspended sediment concentration (M/L^3)
τ = travel time, x/U (T)

The analytical solution above is obviously a gross approximation of reality, but the time-varying nature of the loadings can be preserved and the influence of suspended sediment is accommodated, however simplistically. Because time variation in the loads is preserved, it follows that cdfs can be generated and an estimate of risk is possible. A major shortcoming of the approach is the inability to readily accommodate the influence of bottom sediments. A crude approximation is possible by assuming net transfers as first-order rates, but data on which to base such as empirical approach are virtually nonexistent.

Steady-State Solutions

If risk is to be inferred from time series concentration data, steady-state solutions (i.e., solutions for which $\partial c/\partial t = 0$) are of limited value in exposure assessment. Baughman and Burns (2) argue for use of steady-state equations wherever possible and, for certain boundary conditions and study objectives, this approach has enjoyed considerable success (8,19). For cases where the time variation is caused solely by flow, judicious (piecewise) application of steady-state methods at specific flow conditions may produce useful estimates of risk. In this situation, the concentration frequencies generated are determined largely by flow variations and the problem reduces to one of single-variable probabilities. If other environmental factors (e.g., pH, light, temperature, sediment) are also time varying, then their joint frequencies must be known *a priori* if steady-state models are to be applied even for selected conditions in order to generate reasonable concentration frequency distributions. Steady-state approximations (i.e., the assumption $\partial c/\partial t = 0$) of dynamic systems are most reasonable when the system response to varying inputs is more rapid than the rate of change of the varying inputs. If,

however, the actual inputs that force a system toward a quasi steady-state condition change rapidly, then that steady-state condition will not be achieved. As a result, the system will continually exhibit a transient response, moving toward changing steady state targets.

The first steady-state organic pollutant model was that of Smith et al. (20). More recently, Burns, Cline, and Lassiter (3) developed the Exposure Analysis Modeling System (EXAMS), which uses second-order transformation kinetics for the fate processes described in the previous section and calculates bed sediment-water column interactions by dispersive exchange.

Dynamic Solutions

TOXIWASP (1) is a dynamic chemical and sediment model based on the Water Analysis Simulation Program (WASP) (4). WASP is a general modeling package designed for planning analysis of water quality problems in streams, lakes, reservoirs, and estuaries. Site and pollutant specific models can be formulated with this program by linking it to different water quality kinetic subroutines. WASP uses the compartment modeling approach whereby segments can be arranged in a one-, two-, or three-dimensional configuration. Pollutant transport is based on user-specified flow and dispersive mixing between segments. Although segment volumes are time-constant, all other parameters and forcing functions may vary in space and time. WASP calculates time-varying water quality parameter concentrations using an explicit, backward difference numerical solution to the mass flux form of the one dimensional advective-dispersive equation:

$$\frac{\Delta M_j}{\Delta t} = \sum_{i=1}^{n} [Q_i C_i + E_i A_i \left(\frac{\Delta C}{L}\right)_i] + W_j - KV_j \qquad [9]$$

where ΔM = change in constituent mass
ΔC = change in constituent concentration (M/L^3)
Q = water flow (L^3/T)
E = longitudinal dispersion (L^2/T)
A = cross-sectional area (L^2)
L = characteristic mixing length (L)
W = mass loading (M/T)
K = kinetic degradation or transformation rate ($ML^{-3}T^{-1}$)
V = segment volume (L^3)
subscript "i" = segment number
subscript "j" = adjacent segments
Δ = difference symbol

Because this equation calculates the mass transported through the crosssections A_i, it is termed the "mass flux" form.

TOXIWASP was created from WASP by adding a set of subroutines that calculate chemical degradation (the last term in equation 9) and that calculate special bed sediment transport processes such as sediment-water dispersive exchange, pore water percolation, and net burial-scour. The chemical degradation routines are simplified from the EXAMS kinetic structure (3).

From chemical characteristics of a compound and the environmental parameters of the system, TOXIWASP formulates a total degradation rate. This rate is based on a simple addition of the pseudo-first order rates due to hydrolysis, oxidation, biolysis, volatilization, photolysis, and other processes. Sorption onto sediments and onto biomass is calculated assuming local equilibrium, using a chemical-specific partition coefficient, and spatially varying environmental organic carbon fractions.

TOXIWASP applies equation 9 to calculate sediment and chemical concentrations for every segment, including surface

water, subsurface water, surface bed, and subsurface bed. Sediment is assumed to be a conservative constituent that is advected and dispersed among water segments and that can settle to and scour from bed segments. Within the bed, sediment can be "transported" to lower layers through burial, or to upper layers through erosion. (Bed layers have constant thicknesses, their vertical location is referenced to the bed surface, which rises with deposition or falls with scour.)

As stated above, chemicals undergo a pseudo first-order decay, based on summation of several process rates, some of which are actually second-order. The effective first order decay rate can vary with time and is recalculated as often as necessary throughout a simulation. The chemical is advected and dispersed among water segments and can be transported to the bed by sorption onto sediment and subsequent settling, or by dispersive mixing between the top bed layer and the bottom water layer. Within the bed, a chemical can migrate downward through burial, or migrate upward through erosion or pore water percolation. No lateral migration of a chemical within the bed is allowed.

Also in this study, the Hydrologic Simulation Program--FORTRAN (HSPF) was operated as a dynamic organic chemical pollutant and sediment simulation model. The full HSPF program is a comprehensive package for simulation of watershed hydrology and water quality (9). From knowledge of the time history of rainfall, characteristics of the land surface and prevailing agricultural practices, HSPF predicts the time history of runoff, sediment load, and nutrient and pesticide loads. Based upon these results and information about the chemicals involved and the stream channels in the watershed, HSPF then predicts the time history of water quality and quantity throughout the watershed. These calculations are based on kinematic wave routing and an explicit, backward difference numerical solution to the advective equation:

$$\frac{\partial(AC)}{\partial t} + \frac{\partial(AuC)}{\partial x} = \frac{AW}{V} - AK \qquad [10]$$

where u = advective velocity (L/T) and other terms are as previously defined for equation 9.

The RCHRES module of HSPF, which implements equation 10, was recently modified to handle sediment and chemical interactions with the bed. These routines were simplified from SERATRA (15) to simulate a one-layer bed. Sorption onto three size fractions of sediment is calculated as a linear, reversible process.

HSPF applies equation 10 to calculate sediment and chemical concentrations for every segment and its associated bed in a one-dimensional network. The three size fractions of sediment can be advected between water segments and undergo scour from and deposition to the bed depending on stream sediment transport capacity. Sediment transport capacity may be calculated from an empirical power function of flow or the relationships of Colby or Toffaleti (21). Bed thicknesses and properties vary throughout the simulation.

A number of distinct degradation processes can be specified, including hydrolysis, oxidation, photolysis, volatilization, biodegradation, or a lumped first-order decay rate may be specified. The chemical is advected between water segments and can be transported to the bed either by sorption onto suspended sediment and subsequent settling or by direct sorption to the bed surface. The chemical can reenter the water column by desorption from the bed surface or by scour of bed sediment containing sorbed chemical.

Although HSPF has sophisticated simulation capabilities, its data management and manipulation features make it especially convenient for completing more simplified analyses such as the analytical method described previously (Eq. 18). Indeed, the otherwise tedious task of operating an analytical

method with daily loads was reduced to a straightforward application of HSPS's time series management system.

Bed Sediment-Water Column Exchange Solutions

A very important, but poorly quantified, set of processes governs chemical exchange between the bed and the water column. A chemical may sorb onto suspended sediments and settle with the sediments to the bed, or sorb directly to the bed surface when water concentrations are high. When water concentrations are low, the chemical may desorb from the bed surface. Turnover of the bed surface due to either physical or biological processes accelerates this sorption-desorption process. Diffusion of pore water into overlying water will also exchange dissolved chemicals. Percolation of pore water will move dissolved chemical up through the bed into the water column; infiltration can leach chemical down through the bed.

Because these processes are poorly quantified and variable in both space and time, most chemical models now take a largely empirical approach to sediment-water exchange. HSPF and SERATRA describe the exchange as linear sorption-desorption between dissolved chemical in the overlying water and organic sediment in the bed:

$$EXCH = RSED * KT [KPB * C'_w - C'_b] \qquad [11]$$

where EXCH = net mass exchange (M/T)
RSED = upper layer bed sediment mass (M)
KT = sorption-desorption rate (1/T)
KPB = partition coefficient of the chemical onto bed sediment (L^3_w/M_s)

EXAMS and TOXIWASP describe sediment-water exchange as a dispersion process:

$$EXCH = DISPV\ (C_p' - C_w') + DSPSED * DISPV * S'\ (C_b' - C_s' \frac{KPB}{KPW}) \qquad [12]$$

where DISPV = volumetric fluid dispersion (L_w^3/T)
DSPSED = spatially variable sediment turnover ratio (1.0 in EXAMS)
KPW = partition coefficient of the chemical onto suspended sediment in the water column (L_w^3/M_s)

The volumetric dispersion varies spatially, and is calculated by:

$$DISPV = \frac{SCALE * D_b * A_s * FRW}{L_c} \qquad [13]$$

where D_b = vertical pore water dispersion coefficient (L^2/T)
A_s = surface area (L^2)
FRW = porosity, or volumetric fraction of pore water in the bed
L_c = characteristic mixing length (L)
SCALE = units conversion factor

Because TOXIWASP and EXAMS assume local equilibrium between dissolved and sorbed phases of a chemical in each segment, equation 12 can be rewritten:

$$EXCH = DISPV * \frac{1 + KPB * S'}{KPB} * [C_b' - KPB * C_w'] \qquad [14]$$

where DSPSED = 1.0

Equation 14 is now in the same form as equation 11. Thus, the HSPF-SERATRA sorption-desorption rate KT can be related to the EXAMS-TOXIWASP dispersion rate by equating RSED *KT to DISPV * $[\frac{1+KPB*S'}{KPB}]$ and solving for KT. If one also uses the relationship, RSED = BVOL*S'*FRW, then the solution for KT becomes,

$$KT = \frac{SCALE * D_b * A_s}{BVOL * L_c} \quad \left[\frac{1*KPB*S'}{KPB*S'}\right] \qquad [15]$$

where BVOL = the EXAMS-TOXIWASP bed volume (L^3)

SCALE = a unit conversion factor

= 2.584×10^{-4} when $D_b = m^2/hr$, $A = ft^2$, $L_c = ft$, BVOL = $ft^3 \times 10^6$

L_c = ft

BVOL = $ft^3 \times 10^6$

For chemicals with high partition coefficients, the last term in equation 15 is approximately 1.0, simplifying the expression for KT to:

$$KT = \frac{SCALE * D_b * A_s}{BVOL * L_c} \qquad [16]$$

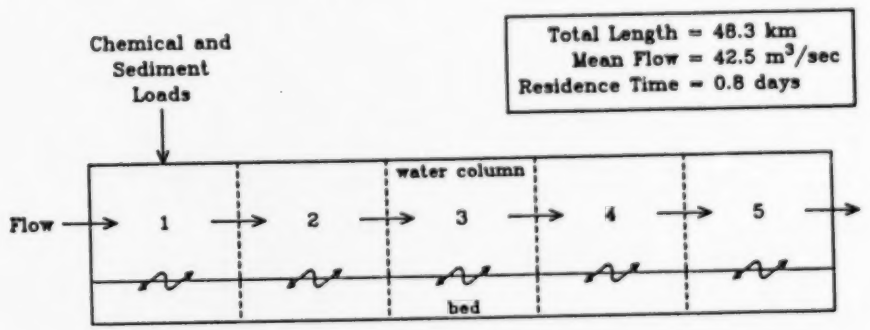
Although the basic sediment-water exchange mechanisms are mathematically equivalent, each model has its own elaborations. The exchange rates are spatially variable in EXAMS and TOXIWASP, and these models include percolation of pore water. TOXIWASP adds spatially variable sediment turnover ratios, spatially variable net bed scour or deposition rates, and settling of suspended sediment. HSPF and SERATRA simulate three sediment size fractions. Scour-deposition and settling are calculated as dynamic processes. SERATRA adds multiple sediment layers, which can be added through deposition or subtracted through erosion. HSPF allows spatially variable sorption-desorption rates. The use of all these mathematical formulations is limited by the lack of good, thorough data necessary to calibrate and test the models on a site-specific basis.

An Example of Alternative Solutions

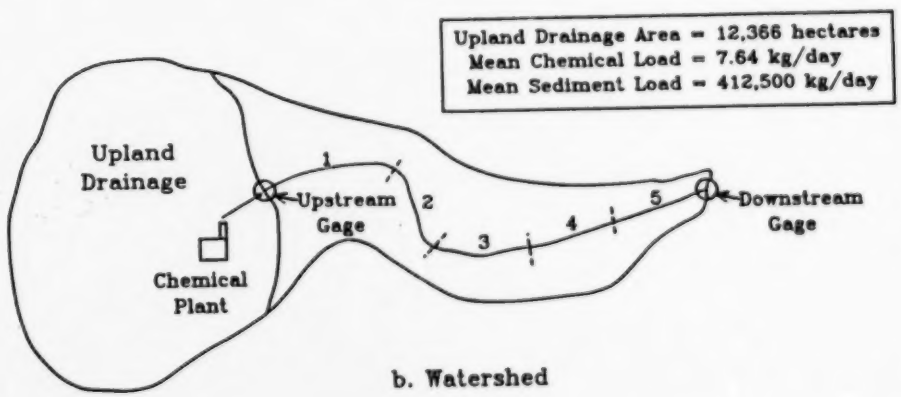
Application of the various models described above remains largely an untested process although various components

have been evaluated for their ability to simulate field observation (19). Much can be learned, however, by applying each model to the range of problems usually encountered in many practical environmental exposure assessments. Results from each model can be evaluated for their relative differences and a better understanding of the various models and their appropriate use can be achieved.

The applications problem selected for this study involves modeling a river reach characterized in Figure 1. Figure 1 actually represents a gaged section of the Yazoo River in the State of Mississippi, USA. Flow records were available for the gages shown in Figure 1b and have been used



a. River



b. Watershed

Figure 1. Overview of river environment.

in previous studies of pesticide exposure within the river basin (16). Flow is shown in Figure 2 for 1972. The chemical and sediment loads for 1972 are also shown in Figure 2 as derived (not measured) from a previous modeling study of pesticide runoff in the area. The annual-average flows and loads are also given in Figure 1.

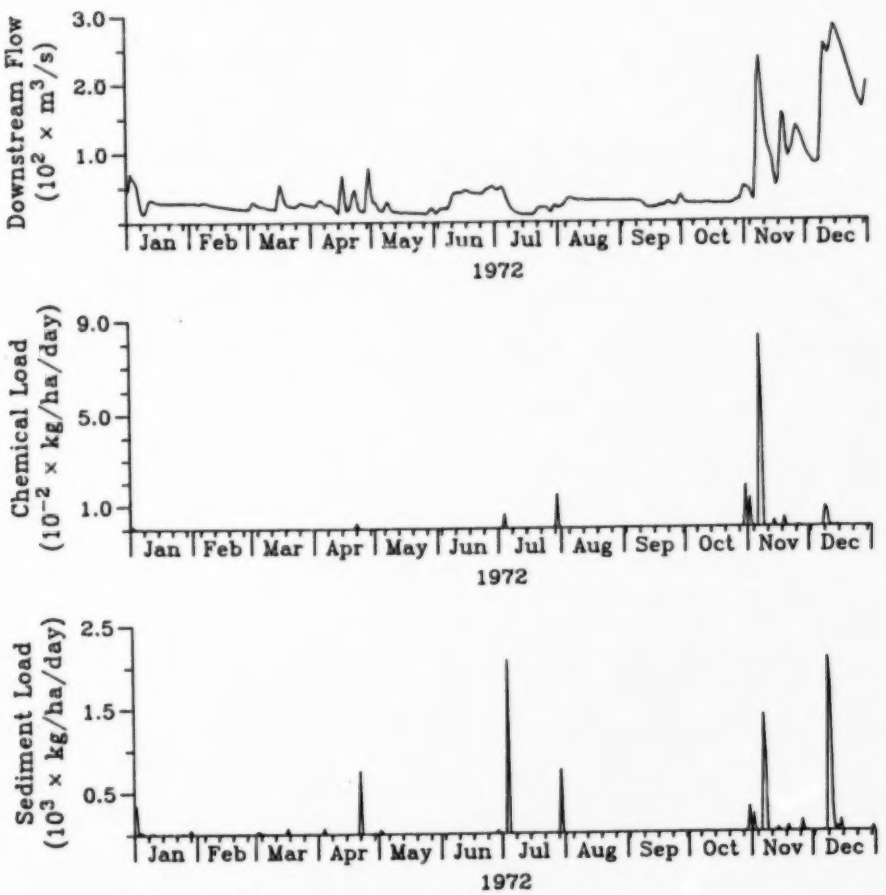


Figure 2. Unsteady loads and flow.

The environment and its characterization in Figures 1 and 2 can be combined with various loading scenarios to generate four general conditions: (1) steady river flow and steady loads represented by mean flows and input loads in Figure 1, (2) steady river flow and dynamic input loads represented by the mean flow in Figure 2 and the dynamic loads in Figure 2, (3) dynamic river flows and steady input loads represented by the flows in Figure 2 and the mean input load in Figure 1, and (4) dynamic river flows and input loads as represented in Figure 2. These four cases can be thought to represent actual real world situations or they can be perceived as possible ways to represent the same situation. For example, the conditions represented by condition 4 could be approximated by the other three conditions for purposes of analysis or modeling.

Another key set of variables that influence results are those related to the chemical properties of the input loads. Recall from previous discussion and from the description of each model that several chemical, biological, and transport processes are chemical-specific and must be uniquely characterized (parameters estimated) for each chemical. To simplify this process, however, one can specify a lumped first-order rate constant for all transformations and further specify a bulk sediment-water partition coefficient. These two parameters capture the chemical-specific information needed for the comparison study intended here. The values chosen for this study for each of two hypothetical chemicals represent a relatively non-persistent compound that sorbs weakly to sediments and a more persistent compound that sorbs much more strongly to sediment.

The range of general conditions and chemicals, and the models investigated for each are summarized in Figure 3. Tables 2-3 give the detailed environmental characteristics required for the various models. Most of these data were derived from gaging information, but some were assumed for

Case	Conditions: Flow	Load	Chemical	Analytical	Models: EXAMS	TOXIWASP	HSPF
1	S	S	1		*		
	S	S	2		*		
2	S	D	1	*		*	
	S	D	2	*		*	
3	D	S	1		*	*	*
	D	S	2		*	*	*
4	D	D	1			*	*
	D	D	2			*	*
5	D	H	1				*
	D	H	2				*

S = steady

D = varying daily

H = varying hourly

1 = high decay (0.2 day^{-1}), low partitioning (KOC = 200 l_w/kg_o)

2 = low decay (0.02 day^{-1}), high partitioning (KOC = 2000 l_w/kg_o)

Figure 3. Conditions investigated by models.

purposes of this study. Note that in Figure 3 five conditions rather than only the four discussed above are given. The last condition accommodates utility of an hourly varying load for comparison with the daily varying load for case 4. Recall from the discussion of each model that some processes included in one are not included in others. Most notable among these is the treatment of bed sediments. The analytical model (equation 8) does not include the influence of bed sediments. Thus, TOXIWASP used in case 2 was configured to omit bed-sediment interactions to enable a more meaningful comparison between the TOXIWASP results and those from the analytical model. Also recall from previous discussion of steady-state

Table 2

Parameter Values for River Simulations

	Segment Number				
Water Sediment Bed	1 2	3 4	5 6	7 8	9 10
Geometry					
Length m	9.66	9.66	9.66	9.66	9.66
Mean Water Volume m^3	5.25×10^5	5.51×10^5	5.80×10^5	6.04×10^5	6.29×10^5
Bed Volume m^3	1.39×10^4	1.39×10^4	1.39×10^4	1.39×10^4	1.39×10^4
Surface Area m^2	2.28×10^5	2.28×10^5	2.28×120^5	2.28×10^5	2.28×10^5
Mean Water Depth m	2.30	2.42	2.54	2.65	2.76
Bed Depth m	0.061	0.061	0.061	0.061	0.061
Transport					
Sediment-Water Dispersion cm^2/sec	6.59×10^{-5}	6.59×10^{-5}	6.59×10^{-5}	6.59×10^{-5}	6.59×10^{-5}
Mean Flow m^3/sec	35.7	39.1	42.5	6.1	9.4
Mean Residence Time days	0.17	0.16	0.16	0.15	0.15
Sediment Characteristics					
Organic Fraction, Water	0.03	0.03	0.03	0.03	0.03
Organic Fraction, Bed	0.06	0.06	0.06	0.06	0.06
Bulk Density, Bed kg/l	2.70	2.70	2.70	2.70	2.70
Bed Porosity	0.50	0.50	0.50	0.50	0.50

Table 3

Channel Properties Used in HSPF Routing

Segment No.	Flow (m^3/s)	Depth (m)	Surface Area (m**2)	Volume (**2)	Flow-Thru Time (days)
	0.1	0.4	111673.	44199.	5.12
	0.5	0.7	138774.	101247.	2.34
	1.0	0.9	152387.	144681.	1.67
	5.0	1.8	189369.	331421.	0.77
1,3,5	10.0	2.3	207945.	473599.	0.55
	50.0	4.2	258410.	1084877.	0.25
	100.0	5.5	283758.	1550283.	0.18
	500.0	10.1	352622.	3551244.	0.08
	1000.0	13.1	387211.	5074707.	0.06
	0.1	0.3	101261.	30557.	3.54
	0.5	0.5	124827.	68437.	1.58
	1.0	0.7	136597.	96852.	1.12
	5.0	1.3	168387.	216917.	0.50
7,9	10.0	1.7	184264.	306979.	0.36
	50.0	3.0	227147.	687532.	0.16
	100.0	3.9	248566.	976991.	0.11
	500.0	7.1	306413.	2179178.	0.05
	1000.0	9.2	335306.	3083959.	0.04

models the conditions for which dynamic systems could be approximated by repeated (piecewise) application of such models. Application of EXAMS to case 3 conditions was accomplished by obtaining steady-state solutions at the selected flow conditions shown in Table 4. These flows span the range of observed flows shown in Figure 2. Because only flow varied in this case and because the variations were not dramatic (flow is regulated by an upstream reservoir), one might expect a piecewise application of a steady-state model to be reasonable practice. Application to other situations where loads and flows are both dynamic is not recommended by the authors.

Investigation of the conditions and models shown in Table 1 allowed comparisons in several ways. For some cases different models were applied to the same condition allowing evaluation of differences in models. Differences in results

Table 4

Flow Frequency Analysis of River Flows

	Segment No.	Frequency 5%	15%	30%	50%	70%	85%	95%
Inlet gage	1	8.5	11.3	19.3	24.1	31.1	46.7	142
	3	9.4	12.5	19.9	24.8	32.5	50.7	153
	5	10.4	13.6	20.6	25.5	33.8	54.7	164
	7	11.3	14.7	21.3	26.2	35.1	58.6	176
	9	12.3	15.9	22.0	26.9	36.4	62.6	187
Outlet gage	0	13.2	17.0	22.7	27.6	37.7	66.5	198

were directly attributable to differences in the models being applied to the same condition. The range of conditions was also selected to examine modeling results under various simplifying assumptions. For example, case 4 can represent an additional assumption imposed on case 5. In other words, the hourly varying loads of case 5 were approximated by the same loads aggregated to daily varying values in case 4. Similarly, case 3 can be viewed as an approximation to case 4 followed by cases 2 and 1. Finally, each condition and model was investigated for each of two chemicals characterized as shown in Figure 2.

Estimation of environmental risk remained the objective for exposure assessment modeling in this study and, therefore, time series concentrations had to be produced by the models in order to generate cumulative probability density functions for the chemicals of interest. The concentration cdf generated from each model simulation was used as the basis for comparing results for each of the conditions and chemicals presented in Figure 3. Each cdf was derived by assigning class intervals, pooling daily average concentrations into each appropriate class interval, and accumulating the totals over the range of simulated values (minimum to maximum).

Results and Discussion

The model results for case 1 cannot be expressed as time series or in terms of cdf's because only steady-state values were estimated. For the other cases, however, time series concentrations for dissolved chemical in the water column and sorbed chemical in the bed were estimated by each model. As stated earlier, EXAMS results for case 3 are not time series *per se*, rather they are specific steady-state solutions to specific flow conditions (see Table 3) that cover the range of flows. Typical results for cases 4 and 5 for each of the two chemicals are shown in Figure 4. The short residence time for

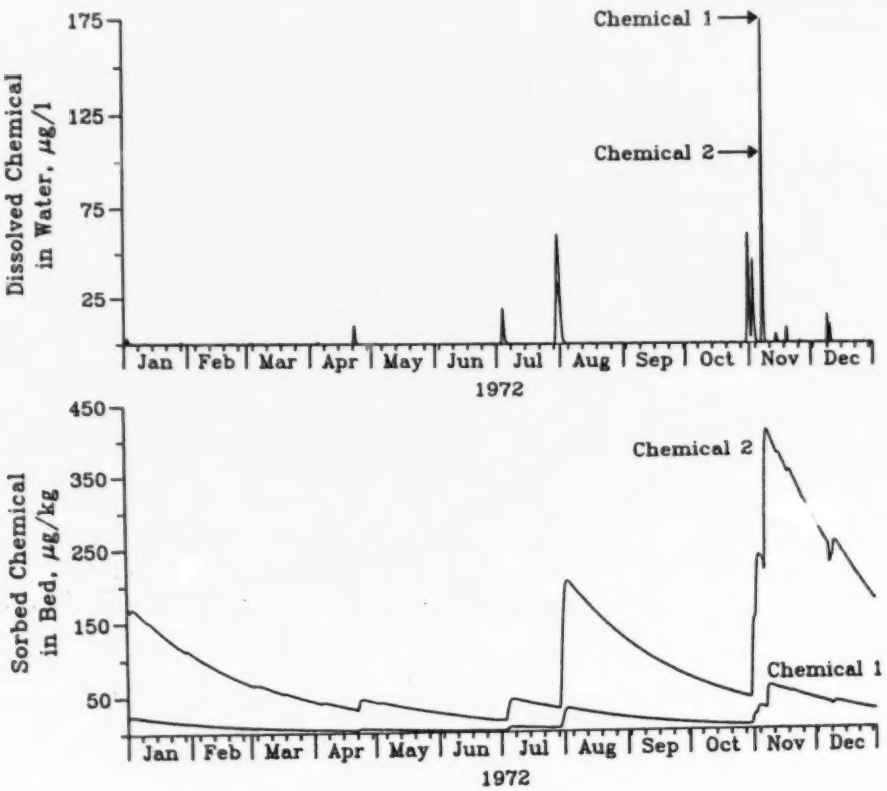


Figure 4. Downstream chemical response to unsteady loads and flow.

the river system precludes a major difference in the concentration profiles as a result of degradation but the differences due to partitioning are more pronounced. This is readily apparent from the bed sediment concentrations shown in Figure 4.

The time-series concentrations of Figure 4 are useful to examine but perhaps more insight can be gained by examining each model output as cumulative frequencies. The cdf's estimated by each model for each of the conditions outlined in Table 2 and for the flow and loading given in Figures 1 and 2 are shown in Figures 5 and 6. Semi-log representations of concentration were used only because the range of values spanned several orders of magnitude.

It is useful to take case 5 as our best estimate of the true cumulative probabability of the chemical concentrations at the downstream gage. Water concentrations below about the 75th percentile result from the desorption of chemical from the bed rather than direct chemical loading. Case 4 predicts slightly higher "chronic" concentrations because average daily events allow more chemical to sorb to the bed than average hourly events, even if the total mass loadings are the same. Higher bed storage during events leads to greater desorption between events. The differences between HSPF and TOXIWASP for case 4 are probably numerical, the result of constant time steps in the former and variable time steps in the latter.

Case 2, featuring constant flow, daily loads, and no bed sediment, mimics cases 4 and 5 above the 95th percentile where concentrations are driven by large loads. Below this percentile, concentrations for case 2 fall progressively lower, lacking desorption. The concentration of zero, not represented on this semilog graph, has a cumulative frequency of about 75%. TOXIWASP (no bed sediment included) predicts slightly higher concentrations than the analytical solution

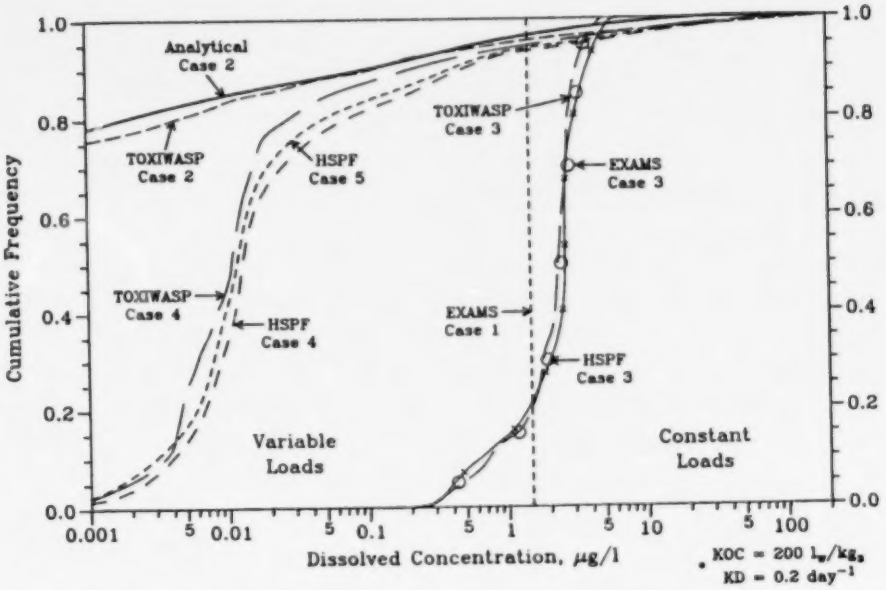


Figure 5. Dissolved chemical 1 in water.

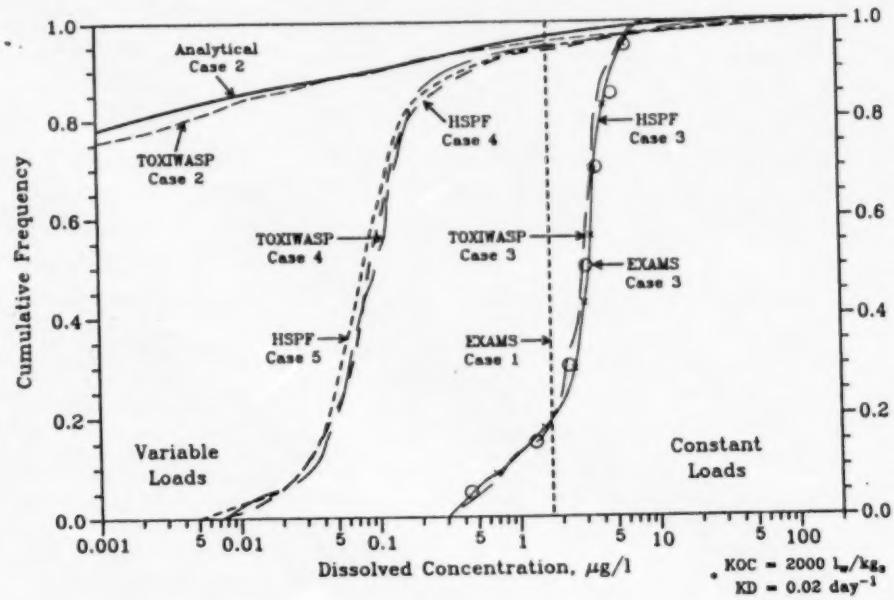


Figure 6. Dissolved chemical 2 in water.

for a given cumulative frequency because of numerical dispersion.

Substituting the constant average loading for the dynamic loading, case 3 results differ remarkably from cases 2, 4, and 5. Concentration variations are due entirely to flow variations. The case 3 results confirm that piecewise steady-state solutions at various flows (EXAMS) can approximate the dynamic system under study if certain conditions are met (e. g., steady loads, gradually varying flows). The true steady-state case 1 concentration is less than the case 3 median because the average yearly flow used was higher than the median flow. The case 3 concentration varies from the mean flow, true steady state concentration by a factor of about $\pm$ 3.

Comparing the two chemicals for each case, we find concentrations for chemical 2 always exceed those for chemical 1. This is primarily due to differences in the decay rate. Dissolved chemical 1 decays at a rapid 0.2 per day rate, whereas dissolved chemical 2 decays at a slower 0.02 per day rate. Referring to Figure 3, note that chemical 2 builds up in the bed to a much greater extent than chemical 1 because its partition coefficient is higher (2000 l/kg versus 200 l/kg). This same factor reduces the dissolved concentrations for chemical 2 during peak events.

Conclusions

Care must be taken in drawing general conclusions from specific studies. Our results should be valid for rivers similar to the moderate-sized reach studied here. Interactions between varying environmental parameters and chemical decay rates, not studied here, can add another dimension of complexity to comparative analyses. Indeed, such conditions may yield vastly different results for some cases, especially

those investigating steady-state approximations to dynamic systems. Based on this limited comparative study, several conclusions were drawn:

1. Steady-state models gave reasonable estimates of the median concentration for the constant load, variable flow situations.

2. Flow variation alone produced concentrations up to a factor of ±3 around steady state values obtained with mean annual flows.

3. Flow conditions taken from the *a priori*, known flow cumulative frequency distribution were successfully used for steady-state approximations of the chemical cumulation frequency distribution for conditions of steady load and varying flow.

4. Steady-state models applied to rivers with pulse loadings were inappropriate.

5. All approaches using non-steady loading gave similar results for the high concentration, infrequent events that could produce acute toxic effects.

6. Analysis of the high concentration, infrequent events did not require modeling interaction with the bed sediment.

7. It was necessary to simulate bed sediment if analysis of low concentrations were desired.

8. The use of daily averaged input loads rather than hourly input loads made only a minor difference in simulation results for low concentrations, and a slightly greater difference for the higher concentrations.

9. Assuming constant river volumes (TOXIWASP) rather than time-variable volumes (HSPF) resulted in no substantial differences between the respective cumulative frequency distributions.

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